

Synthesis of cuprate superconductors*

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Abstract. There has been unprecedented activity pertaining to the synthesis and characterization of superconducting cuprates in the last few years. A variety of synthetic strategies has been employed to prepare pure monophasic cuprates of different families with good superconducting properties. Besides the traditional ceramic method, other methods such as coprecipitation and precursor methods, the sol-gel method, the alkali flux method and the combustion method have been employed for the synthesis of cuprates. Depending on the requirements, varying conditions such as high oxygen or hydrostatic pressure and low oxygen fugacity are employed in the synthesis. In this review, we discuss the synthesis of the various types of cuprate superconductors and point out the advantages and disadvantages of the different methods. We have provided the necessary preparative details, presenting the crucial information in tabular form wherever necessary.

1. Introduction

Since the discovery of high- T_c superconductivity in the La-Ba-Cu-O system [1], a variety of cuprate superconductors with T_c s going up to 128 K have been synthesized and characterized [2, 3]. No other class of materials has been worked on so widely and intensely in recent years as have the cuprate superconductors. Several methods of synthesis have been employed for preparing the cuprates, with the objective of obtaining pure monophasic products with good superconducting characteristics [3, 4]. The most common method of synthesis of cuprate superconductors is the traditional ceramic method which has been employed for the preparation of a large variety of oxide materials [5]. Although the ceramic method has yielded many of the cuprates with satisfactory characteristics, different synthetic strategies have become necessary in order to control factors such as the cation composition, oxygen stoichiometry, cation oxidation states and carrier concentration. Specially noteworthy amongst these methods are chemical or solution routes which permit better mixing of the constituent cations in order to reduce the diffusion distances in the solid state [5, 6]. Such methods include coprecipitation, use of precursors, the sol-gel method and the use of alkali fluxes. The combustion method or self-propagating high-temperature synthesis (SHS) has also been employed. In this review, we will discuss the preparation of cuprate superconductors by the different methods, mentioning

the special features of each method and the conditions employed for the synthesis. In table 1, we give a list of the cuprate superconductors discussed in this review along with their structural parameters and approximate T_c values. Preparative conditions such as reaction temperature, oxygen pressure, hydrostatic pressure and annealing conditions are specified in the discussion and given in tabular form where necessary. It is hoped that this review will be found useful by practitioners of the subject as well as those freshly embarking on the synthesis of these materials.

2. Ceramic method

The most common method of synthesizing inorganic solids is by the reaction of the component materials at elevated temperatures. If all the components are solids, the method is called the ceramic method [5]. If one of the constituents is volatile or sensitive to the atmosphere, the reaction is carried out in sealed evacuated capsules. Platinum, silica or alumina containers are generally used for the synthesis of metal oxides. The starting materials are metal oxides, carbonates, or other salts, which are mixed, homogenized and heated at a given temperature sufficiently long for the reaction to be completed. A knowledge of the phase diagram is useful in fixing the composition and conditions in such a synthesis.

The ceramic method generally requires relatively high temperatures (up to 2300 K) which are generally attained by resistance heating. Electric arc and skull

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Table 1. Structural parameters and approximate T_c values of cuprate superconductors.

Cuprate	Structure	T_c (K) (max. value)
1 $\text{La}_2\text{CuO}_{4+x}$	Bmab; $a = 5.355, b = 5.401, c = 13.15 \text{ \AA}$	39
2 $\text{La}_{2-x}\text{Sr}_x(\text{Ba})\text{CuO}_4$	I4/mmm; $a = 3.779, c = 13.23 \text{ \AA}$	35
3 $\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.825, c = 19.42 \text{ \AA}$	60
4 $\text{YBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.821, b = 3.885, c = 11.676 \text{ \AA}$	93
5 $\text{YBa}_2\text{Cu}_4\text{O}_8$	Ammm; $a = 3.84, b = 3.87, c = 27.24 \text{ \AA}$	80
6 $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$	Ammm; $a = 3.851, b = 3.869, c = 50.29 \text{ \AA}$	93
7 $\text{Bi}_2\text{Sr}_2\text{CuO}_8$	Amaa; $a = 5.362, b = 5.374, c = 24.622 \text{ \AA}$	10
8 $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	A2aa; $a = 5.409, b = 5.420, c = 30.93 \text{ \AA}$	92
9 $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_2\text{O}_{10}$	A2aa; $a \sim 5.39, b \sim 5.40, c \sim 37 \text{ \AA}$	110
10 $\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$	P4/mmm; $a = 3.888, c = 17.28 \text{ \AA}$	25
11 $\text{Ti}_2\text{Ba}_2\text{CuO}_8$	A2aa; $a = 5.468, b = 5.472, c = 23.238 \text{ \AA};$ I4/mmm; $a = 3.866, c = 23.239 \text{ \AA}$	92
12 $\text{Ti}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.855, c = 29.318 \text{ \AA}$	119
13 $\text{Ti}_2\text{Ca}_2\text{Ba}_2\text{Cu}_2\text{O}_{10}$	I4/mmm; $a = 3.85, c = 35.9 \text{ \AA}$	128
14 $\text{Ti}(\text{BaLa})\text{CuO}_5$	P4/mmm; $a = 3.83, c = 9.55 \text{ \AA}$	40
15 $\text{Ti}(\text{SrLa})\text{CuO}_5$	P4/mmm; $a \sim 3.7, c \sim 9 \text{ \AA}$	40
16 $(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CuO}_5$	P4/mmm; $a = 3.738, c = 9.01 \text{ \AA}$	40
17 $\text{TiCaBa}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.856, c = 12.754 \text{ \AA}$	103
18 $(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{CaSr}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80, c = 12.05 \text{ \AA}$	90
19 $\text{TiSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80, c = 12.10 \text{ \AA}$	90
20 $\text{TiCa}_2\text{Ba}_2\text{Cu}_2\text{O}_8$	P4/mmm; $a = 3.853, c' = 15.913 \text{ \AA}$	110
21 $(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_9$	P4/mmm; $a = 3.81, c = 15.23 \text{ \AA}$	120
22 $\text{TiBa}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_8$	I4/mmm; $a \sim 3.8, c \sim 29.5 \text{ \AA}$	40
23 $\text{Pb}_2\text{Sr}_2\text{Ln}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_8$	Cmmm; $a = 5.435, b = 5.463, c = 15.817 \text{ \AA}$	70
24 $\text{Pb}_2(\text{Sr}, \text{La})_2\text{Cu}_2\text{O}_8$	P2 ₂ 1 ₂ ; $a = 5.333, b = 5.421, c = 12.609 \text{ \AA}$	32
25 $(\text{Pb}, \text{Cu})\text{Sr}_2(\text{Ln}, \text{Ca})\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.820, c = 11.826 \text{ \AA}$	50
26 $(\text{Pb}, \text{Cu})(\text{Sr}, \text{Eu})(\text{Eu}, \text{Ce})\text{Cu}_2\text{O}_7$	I4/mmm; $a = 3.837, c = 29.01 \text{ \AA}$	25
27 $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	I4/mmm; $a = 3.95, c = 12.07 \text{ \AA}$	30
28 $\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	P4/mmm; $a = 3.902, c = 3.35 \text{ \AA}$	110
29 $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	P4/mmm; $a = 3.942, c = 3.393 \text{ \AA}$	40

techniques give temperatures up to 3300 K while high-power CO_2 lasers give temperatures up to 4300 K. The main disadvantages of the ceramic method are the following:

(i) The starting mixtures are inhomogeneous at the atomic level.

(ii) When no melt is formed during the reaction, the entire reaction has to occur in the solid state, first by a phase boundary reaction at the points of contact between the components and later by the diffusion of the constituents through the product phase. With the progress of the reaction, diffusion paths become longer and the reaction rate slower; the reaction can be speeded up to some extent by intermittent grinding between heating cycles.

(iii) There is no simple way of monitoring the progress of the reaction. It is by trial and error that one decides on the appropriate conditions required for the completion of the reaction. Because of this difficulty, with the ceramic method one often ends up with mixtures of reactants and products. Separation of the desired products from such mixtures is difficult, if not impossible.

(iv) Frequently it becomes difficult to obtain a compositionally homogeneous product even where the reaction proceeds nearly to completion.

Despite the above limitations, the ceramic method is widely used for the synthesis of a large variety of inorganic solids. In the case of the cuprate superconductors,

the ceramic method involves mixing and grinding the component oxides, carbonates or other salts, and heating the mixture, generally in pellet form, at the desired temperature. A common variation of the method is to heat a mixture of nitrates obtained by digesting the metal oxides/carbonates in concentrated HNO_3 and evaporating the solution to dryness. Heating is carried out in air or in an appropriate atmosphere, controlling the partial pressure of oxygen where necessary. In the case of thallium cuprates, because of the volatility and poisonous nature of the thallium oxide vapour, reactions are carried out in sealed tubes. In some of the earlier preparations, the thallium cuprates were synthesized in open furnaces. This is however, not recommended. A successful synthesis by the ceramic method depends on several factors which include the nature of the starting materials (the choice of oxides, carbonates), the homogeneity of the mixture of powders, the rate of heating as well as the reaction temperature and duration.

2.1. La_2CuO_4 -related 214 cuprates

Synthesis of alkaline-earth-doped $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{Ca}, \text{Sr}$ and Ba) of K_2NiF_4 structure with superconducting transition temperatures up to 35 K is readily achieved by the ceramic method. Typically, the synthesis is carried out by reacting stoichiometric quantities of the oxides and/or carbonates around 1300 K in

oxygen atmosphere at 0.5 A after the sintering step [10]. Metal nitrates have also been used as the starting materials for the synthesis [11–13]. By starting with metal nitrates, one obtains a more homogeneous starting mixture, since the hydrated metal nitrates have low melting points leading to a uniform melt in the initial stage of the reaction. Furthermore, nitrates provide an oxidative atmosphere, which is required to obtain the necessary oxygen content.

Stoichiometric La_2CuO_4 is an antiferromagnetic insulator. La_2CuO_4 prepared under high oxygen pressures, however, shows superconductivity ($T_c \sim 35$ K) since the oxygen excess introduces holes just as the alkaline earth dopants [14–16]. $\text{La}_2\text{CuO}_{4+\delta}$ (δ up to 0.05) has been synthesized by annealing La_2CuO_4 under an oxygen pressure of 3 kbar at 870 K [14, 15] or 23 kbar at 1070 K [16]. Oxygen plasma has also been used to increase the oxygen content.

The next homologue of La_2CuO_4 containing two Cu–O layers, $\text{La}_{1.6}\text{Sr}_{0.4}\text{CaCu}_2\text{O}_6$ ($T_c \sim 60$ K), has been synthesized by using high oxygen pressures [17]. The synthesis involves heating the sample at an oxygen pressure of around 20 bar at 1240 K. The material prepared at ambient oxygen pressures (in air) is an insulator. Several other high-oxygen-pressure preparations have been reported on the $n=2$ member of the $\text{La}_{n+1}\text{Cu}_{2n}\text{O}_{2n+3}$ homologous series by making use of commercially available high-pressure furnaces [18, 19]. In table 2, we have summarized the preparative conditions for 123 and related cuprate superconductors.

2.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$ and other 123 cuprates

Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with the orthorhombic structure can be easily prepared by the ceramic method. Most of the investigations of the 123 compound, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been carried out on the materials prepared by reacting Y_2O_3 and CuO with BaCO_3 [20, 21]. It is noteworthy that Rao *et al* [21] obtained monophasic $\text{YBa}_2\text{Cu}_3\text{O}_7$ as the $x=1.0$ member of the $\text{Y}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14}$ series. In the method employed for preparing $\text{YBa}_2\text{Cu}_3\text{O}_7$, stoichiometric quantities of high-purity Y_2O_3 , BaCO_3 and CuO are ground thoroughly and heated initially in powder form around 1223 K for a period of 24 h. Following the calcination step, the powder is ground, pelletized and sintered at the same temperature for another 24 h. Finally, annealing is carried out in an atmosphere of oxygen around 773 K for 24 h to obtain the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ phase showing 90 K superconductivity. Oxygen annealing has to be carried out below the orthorhombic tetragonal transition temperature (~ 960 K); tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0.6 \leq \delta \leq 1.0$) is not superconducting. Intermittent grinding is necessary to obtain monophasic, homogeneous powders. This kind of complex heating schedule often gives rise to microscopic compositional inhomogeneities. Furthermore, CO_2 released from the decomposition of BaCO_3 can react with $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to form non-superconducting

the evolution of CO_2 during the synthesis is to use BaO_2 instead of BaCO_3 [23]. Some of the impurities or side products in the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ are BaCuO_2 , Y_2BaCuO_5 and $\text{Y}_2\text{Cu}_2\text{O}_5$ [24]. The ternary phase diagram given in figure 1 illustrates the complexities of this cuprate system.

Using BaO_2 as the starting material has two advantages. It has a lower decomposition temperature than BaCO_3 and the 123 compound is therefore formed at relatively low temperatures. BaO_2 acts as an internal oxygen source and the duration of annealing in an oxygen atmosphere is reduced to a considerable extent. Sharp superconducting transitions are observed in samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ made using BaO_2 . Slight excess of copper in the ceramic method is reported to give cuprates with sharper transitions [25]. Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is accomplished in a shorter period if one employs metal nitrates as the starting materials [13, 23]. In table 2, we present the conditions employed for preparing 123 cuprates by the ceramic method.

Other rare-earth cuprates of the 123 type, $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$, where $\text{Ln} = \text{La, Nd, Sm, Eu, Gd, Dy, Ho, Er}$ and Tm (all with T_c values around 90 K) have also been prepared by the ceramic method [26, 27]. Oxygen annealing of these cuprates should also be carried out below the orthorhombic–tetragonal transition temperature [3]: La, 754 K; Nd, 837 K; Gd, 915 K; Er, 973 K; Yb, 976 K etc. Nearly 30% of Y can be substituted by Ca in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, retaining the basic crystal structure [28]; the T_c decreases with the increase in calcium content. Both La and Sr can be substituted at the Ba site in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [29–31]. With La, monophasic products are obtained for $0 \leq x \leq 1.0$ in $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$, the T_c decreasing with increase in x . In the case of Sr substitution, monophasic products are obtained for $0 \leq x \leq 1.25$ in $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$; high T_c is retained up to $x=1.0$. Ceramic methods have also been used to prepare $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-\delta}$ solid solutions, where M generally stands for a transition element of the first series. In most

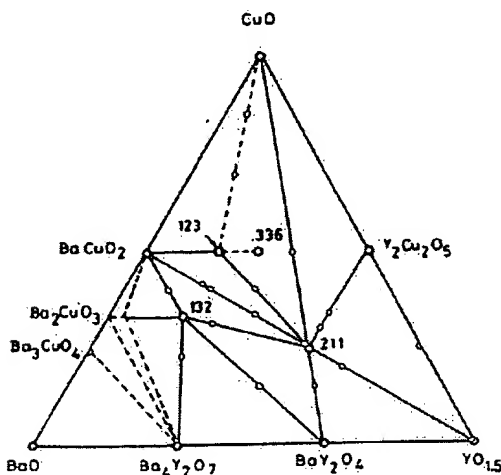


Figure 1. Phase diagram of the Y_2O_3 – BaO – CuO system at 1220 K (from [24]).

Table 2. Preparative conditions for the synthesis of 214, 123, 124 and 247 type cuprates by the ceramic method.

Compound	Starting materials	Preparative conditions			Comments	T_c (K)	Ref.
		Temp. (K)	Time	Gas			
$\text{La}_2\text{CuO}_{4+x}$	$\text{La}_2\text{O}_3, \text{CuO}$	1273 873	24 h 12-48 h	air O_2	3 kbar pressure	35 40	[15] [10]
$\text{La}_{2-x}\text{Sr}_x(\text{Ba}_y)\text{CuO}_4$	$\text{La}_2\text{O}_3, \text{Sr/BaCO}_3, \text{CuO}$ $\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}, \text{Sr/Ba}(\text{NO}_3)_2$ $\text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	1393 1273 873	36 h 20 h 16 h	O_2 air O_2		32	[13]
$\text{La}_{1.8}\text{Sr}_{0.4}\text{CaCu}_2\text{O}_6$	$\text{La}_2\text{O}_3, 10\text{H}_2\text{O}, \text{Sr}(\text{NO}_3)_2$ $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}, \text{CuO}$	1173 1196 1243 1223	3 d 3 d 2 d 2 d	O_2 O_2 O_2 air		60	[17]
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ^a	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	773 1196 723	1 d 2 d 1 d	O_2 air O_2	20 atm	88	[20]
$\text{YBa}_2\text{Cu}_4\text{O}_{10}$ ^b	$\text{Y}_2\text{O}_3, \text{BaO}_2, \text{CuO}$	1173	18 h	air		88	[22]
	$\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}, \text{Ba}(\text{NO}_3)_2$ $\text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	1223	1 h	O_2		80	[13]
	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1313	—	O_2	400 bar	81	[34]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$	1023	1 d	O_2	124 major phase + BaCuO ₂ impurity	77	[35]
	volumes of Na_2CO_3 or K_2CO_3	1073	3 d	O_2	124 major phase + BaCuO ₂ + Y ₂ BaCuO ₅	78	[36, 38]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$ + 0.2M NaNO ₃ or KNO ₃ or Na ₂ O ₂	1073	3 d	O_2	124 major phase + BaCuO ₂ + Y ₂ BaCuO ₅	78	[38]
$\text{Y}_2\text{Ba}_2\text{Cu}_7\text{O}_{10}$ ^c	$\text{Y}_2\text{O}_3, \text{BaCuO}_2, \text{CuO}$	1073	1 d	air	124 single phase	79	[40]
	$\text{Y}_2\text{O}_3, \text{BaCuO}_2, \text{CuO}$ + 0.2M NaNO ₃ + 10 drops of dilute HNO ₃	1088	2 d	O_2		75	[39]
	$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}, \text{CuO}$	1088	10 d	O_2		90	[50]
	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1203	3 d	O_2	124 major phase + BaCuO ₂	90	[36]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$	1133	8 h	O_2	19 bar	90	[36]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$ + 0.2M NaNO ₃	1133	5 d 4 d	O_2 O_2	Single phase	90	[36]

^a Other rare-earth derivatives of the type $\text{LnBa}_2\text{Cu}_3\text{O}_7$ are also prepared by this method. Oxygen annealing is carried out below the orthorhombic-tetragonal transition temperature [26, 27].

^b Other rare-earth derivatives of the type $\text{LnBa}_2\text{Cu}_4\text{O}_{10}$ are obtained by a similar procedure [36, 40].

^c Other rare-earth derivatives of the type $\text{Ln}_2\text{Ba}_2\text{Cu}_7\text{O}_{10}$ are prepared by a similar procedure [36, 38].

2.3. $\text{YBa}_2\text{Cu}_3\text{O}_x$ (124), $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ (247) and related cuprates

The first bulk synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_x$ was reported by Karpinski *et al* [34] who heated the mixture of oxides at 1313 K, under an oxygen pressure of 400 bar. Synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_x$ by the conventional ceramic method without the use of high oxygen pressure suffered from some limitations due to kinetic factors. Cava *et al* [35] found that additives such as alkali carbonates enhance the reaction rate. The procedure involves two steps. In the first step Y_2O_3 , $\text{Ba}(\text{NO}_3)_2$ and CuO are mixed in the stoichiometric ratio and heated at 1023 K for 16–24 h in an oxygen atmosphere. In the second step, the pre-reacted powder is ground with an approximately equal volume of either Na_2CO_3 or K_2CO_3 powder and pellets of the resulting mixture are heated at 1073 K in flowing oxygen for 3 days. After the reaction, the product is washed with water to remove the excess alkali carbonate and dried by gentle heating in air. The product after this step has $\text{YBa}_2\text{Cu}_3\text{O}_x$ as the majority phase (T_c , 77 K) with little BaCuO_2 impurity. Other reaction rate enhancers such as NaNO_3 , KNO_3 , dilute HNO_3 and Na_2O_2 have also been used successfully (in small quantities) to prepare $\text{YBa}_2\text{Cu}_3\text{O}_x$ [36–38]. The 124 cuprate can also be prepared without the addition of a rate enhancer by the solid state reaction of Y_2O_3 , BaCuO_2 and CuO at 1088 K in flowing oxygen [36]. Synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_x$ from the solid state reaction between $\text{YBa}_2\text{Cu}_3\text{O}_7$ and CuO in flowing oxygen has also been reported [39]. The synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_x$ by the ceramic method generally takes a long time and requires repeated grinding and pelletizing.

Other rare-earth 124 cuprates, $\text{LnBa}_2\text{Cu}_3\text{O}_x$ with $\text{Ln} = \text{Eu, Gd, Dy, Ho}$ and Er have been prepared by the ceramic method under an oxygen pressure of 1 atm [36, 40]. The T_c of these cuprates decreases with the increasing ionic radius of the rare earth. Calcium can be substituted at the Y site up to 10% in $\text{YBa}_2\text{Cu}_3\text{O}_x$, and the T_c increases from 79 K to 87 K in such substituted $\text{YBa}_2\text{Cu}_3\text{O}_x$ [41]. Lanthanum can be substituted for barium in $\text{YBa}_2\text{Cu}_3\text{O}_x$ [42]. Single phases of $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_x$ have been obtained for $0 \leq x \leq 0.4$ with the T_c decreasing with increase in x .

Extensive studies have been carried out on the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_x$ under high oxygen pressures [43, 44]. The P - T phase diagram of 124, 123 and 247 cuprates is shown in figure 2. High-oxygen pressure synthesis essentially involves the solid state reaction followed by sintering under high oxygen pressures. The typical sintering temperature and the pressure at which synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_x$ has been carried out are 1200 K and 120 atm of oxygen (for 8 h). By the use of high oxygen pressures [45], it is possible to prepare 124 compounds with other rare earths such as Nd and Sm , which is otherwise not possible under ambient pressures.

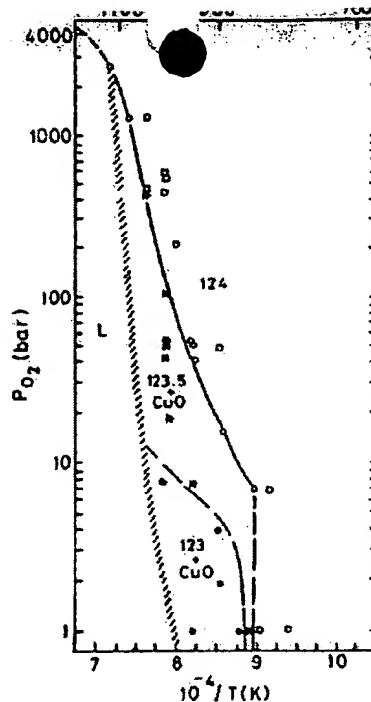


Figure 2. Phase diagram of the 124, 247 and 123 cuprates (from [43]).

A variety of substitutions has been carried out at the Y, Ba and Cu sites in $\text{YBa}_2\text{Cu}_3\text{O}_x$ under high oxygen pressures. Yttrium can be substituted up to 10% by Ca in $\text{YBa}_2\text{Cu}_3\text{O}_x$ giving a T_c of ~ 90 K [46]; 20% Ba has been substituted by Sr without affecting the T_c [47]. Single-phase iron-substituted $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_x$ ($0 \leq x \leq 0.05$) has been prepared at an oxygen pressure of 200 bar [48]; the T_c falls monotonically with increasing iron concentration.

Bordet *et al* [49] first reported the preparation of $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ under oxygen pressures of 100–200 bar. It was soon realized that $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ can be synthesized by the ceramic method under an oxygen pressure of 1 atm by a procedure similar to that employed for $\text{YBa}_2\text{Cu}_3\text{O}_x$, except for the difference in the sintering temperature [36]. There is a narrow stability region between 1123 K and 1143 K for the 247 cuprate to be synthesized under 1 atm oxygen pressure. The best sintering temperature at which the 247 cuprate is formed is 1133 K. Other rare-earth 247 cuprates, $\text{Ln}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ ($\text{Ln} = \text{Dy, Er}$), can also be prepared by this method [36, 38]. About 5% of Y can be replaced by Ca in $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$, and the T_c increases to 94 K [42]. Substitution of La at the Ba site is limited to $\sim 10\%$ in $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$, where the T_c decreases continuously with increasing lanthanum content [42].

Synthesis of 247 cuprates by the high-pressure oxygen method is generally carried out at 1203 K at an oxygen pressure of around 19 bar (for 8 h). This step is followed by slow cooling (typically 5°C min^{-1}) to room temperature at the same pressure [50]. Other rare-earth 247 compounds, $\text{Ln}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ ($\text{Ln} = \text{Eu, Gd, Dy, Ho}$

Figure 4. Section through the phase diagram of the $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$ system at a constant CuO content of 28.6 mol% (from [62]).

semi-wet method involves the solid state reaction between two precursors which are precipitated separately. For example, in the preparation of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, a precipitate of Pb, Sr and Ca (as carbonates) and one of Bi and Cu (as oxalates) are reacted at 1138 K in air for a minimum period of 72 h. The duration of the reaction for the formation of 2223 phase is drastically reduced by this method.

The starting composition of the reactant materials plays an important role in the synthesis of these cuprates. For example, strontium deficiency in the $n = 1$ (2201) member favours monophasic compositions [59, 61]. Strontium deficiency also helps in obtaining a phase-pure $n = 2$ (2122) member [70]. Starting with a 4:3:3:4 stoichiometry of Bi:Ca:Sr:Cu, it has been possible to obtain a monophasic 2122 member [54, 71]. The $n = 3$ (2223) phase, on the other hand, is either obtained through the substitution of Bi by Pb (up to 25%) or by taking an excess of Ca and/or Cu [63–66, 72]. The problem of balancing between phase purity and high T_c of the cuprate gives rise to some difficulty in the synthesis of these cuprates. The coexistence of some of the members of the homologous series, especially in the form of polytypic intergrowths of different layered sequences, is also a problem. This problem is also encountered with thallium cuprates [73, 74].

The $n = 4$ phase, $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Ca}_3\text{Sr}_2\text{Cu}_4\text{O}_{12}$, which was observed in an electron micrograph along with $n = 3$ phase as an intergrowth, was synthesized in bulk by Rao *et al* [75] (with a small proportion of the $n = 3$ phase) by the ceramic method. The $n = 4$ phase has a slightly lower T_c (103 K), than the $n = 3$ phase. This cuprate has also been prepared by Losch *et al* [75].

A variety of substitutions has been carried out in superconducting bismuth cuprates employing the ceramic method [58, 76–79]; some of them are noteworthy. For example, the simultaneous substitution of Bi by Pb and Sr by La in $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ results in a modulation-free superconductor of the formula $\text{BiPbSr}_{1-x}\text{La}_x\text{CuO}_6$ with T_c increased to 24 K [77]. Similarly, co-substitution of Bi by Pb and Ca by Y in the $n = 2$ member (2122) gives a modulation-free superconductor, $\text{BiPbY}_{0.5}\text{Ca}_{0.5}\text{Sr}_2\text{Cu}_2\text{O}_8$ with a T_c of 85 K [77]. Rare-earth substitution for Ca in $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ causes the T_c to go up to 100 K without the introduction of the $n = 3$ phase [58, 78]. As mentioned earlier, the $n = 3$ phase is stabilized by the partial substitution of lead in place of bismuth [63–65]. Another significant discovery is the iodine intercalation of the Bi-2122 superconductor [80]. Intercalation does not greatly affect the superconducting properties of the material; clearly, superconductivity is confined to the two-dimensional CuO_2 sheets in these materials.

Synthesis of a new series of superconducting cuprates of the general formula $\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$ (Bi-2222 phase with Ln = Sm, Eu, Gd) containing a fluorite-like $(\text{Ln}_{1-x}\text{Ce}_x)_2\text{O}_2$ layer between the two CuO_2 sheets has been possible by the ceramic method [81]. Partial substitution of bismuth by lead increases

stability of the 2222 structure with other rare earths [82].

As mentioned earlier, one does not start with an exact stoichiometric composition to obtain the desired final product in the case of superconducting bismuth cuprates. Although structural studies (see for example [84]) indicate the presence of bismuth atoms over strontium and calcium sites as well, it is not possible to prescribe an exact initial composition to obtain the desired final stoichiometry. For example, starting from a nominal composition of $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{SrCaCu}_2\text{O}_9$, one ends up with the formation of the $n = 3$ (2223) member [65]. Therefore, for the purpose of characterizing the various members of the superconducting bismuth cuprates, one starts with some arbitrary composition and varies the synthetic conditions suitably to obtain the desired final product in pure form. The actual compositions of the final cuprate are quite unexpected (e.g. $\text{Bi}_{1.83}\text{Pb}_{0.30}\text{Sr}_{2.04}\text{Ca}_{1.69}\text{Cu}_3\text{O}_9$) as found from analytical electron microscopy [85]. In table 3 we have summarized the preparative conditions of all the members of $\text{Bi}_2(\text{Ca, Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4+x}$ family.

2.5. Thallium cuprates

The conventional ceramic method employed for the synthesis of 214, 123 and bismuth cuprates has to be modified in the case of thallium cuprates of the $\text{Tl}_2\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+4}$, $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$ and $\text{TlCa}_{n-1}\text{Sr}_2\text{Cu}_n\text{O}_{2n+3}$ families due to the toxicity and volatility of thallium oxide. In the early days, the reaction was carried out in an open furnace in air or oxygen atmosphere at high temperatures (1150–1180 K) for 5–10 min [86, 87]. In a typical procedure, the mixture of reactants in the form of a pellet was quickly introduced into the furnace maintained at the desired temperature. Since melt-solid reactions take place faster than solid-solid reactions, the product was formed quickly by this method [87]. Although this method requires a very short duration of heating, it results in the loss of thallium, leading to the danger of inhaling thallium oxide vapour. Some workers have taken certain precautions not to release the Tl_2O_3 vapour into the open laboratory, but the method is still not recommended. Furthermore, the formation of the desired phase is not ensured under the open reaction conditions. Synthesis of thallium cuprates has therefore been carried out in closed containers (sealed tubes) by most workers. By this method, both polycrystalline samples and single crystals can be prepared, since the reaction is carried out over longer periods. Better control of stoichiometry, homogeneity of phases and the total avoidance of the inhalation of toxic thallium oxide vapours are some of the advantages of carrying out sealed tube reactions.

Closed reaction conditions have been achieved in different ways. The reactant mixture is sealed in gold [88] or silver tubes [89] or in a platinum [90] or nickel

Table 3. Preparative conditions for the synthesis of bismuth cuprates by the ceramic method.

Starting composition	Conditions ^a		Product	T_c (K)	Ref.
	Temp. (K)	Time			
$\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_x$	1103	2 d	2201 major phase	20	[51]
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	1123	1 d	2201 major phase	9	[57]
$\text{Bi}_{2.1}\text{Sr}_{1.9}\text{CuO}_6$	1123	2 d	Single phase	10	[59, 61]
$\text{BiPbSr}_{1-x}\text{La}_x\text{CuO}_6$	1150	1 d	Single phase	24	[77]
$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	1103	5 d	Single phase	85	[61]
$\text{Bi}_2\text{Ca}_{1.5}\text{Sr}_{1.5}\text{Cu}_2\text{O}_8^b$	1103	3 d	2122 major phase	80	[53]
$\text{Bi}_4\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_8$	1108	2 d	2122 single phase	85	[71]
$\text{Bi}_2\text{Sr}_{1-x}\text{CaCu}_2\text{O}_8$	1113	3 d	2122 single phase	85	[70]
$\text{BiPbSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_8$	1200	1 d	2122 single phase	85	[77]
$\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Ca}_2\text{Sr}_2\text{Cu}_2\text{O}_8^b$	1140	5 d	2223 major phase	120	[55]
$\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Ca}_{2.5}\text{Sr}_{1.5}\text{Cu}_3\text{O}_8^b$	1100	4 d	2223 major phase	105	[64]
$\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_8$	1153	10 d	2223 single phase	110	[72]
$\text{Bi}_{0.7}\text{Pb}_{0.3}\text{SrCaCu}_{1.8}\text{O}_8$	1153	5 d	2223 major phase	105	[65]
$\text{BiCaSrCu}_2\text{O}_8$	1143	5 d	2223 major phase	120	[65]
$\text{Bi}_{3.2}\text{Pb}_{0.8}\text{Ca}_5\text{Sr}_4\text{Cu}_7\text{O}_8$	1133	5 d	2223 major phase	108	[64]
$\text{Bi}_2\text{Gd}_{1-x}\text{Ce}_x\text{Sr}_3\text{Cu}_2\text{O}_{10}$	1273	10 h	2222 single phase	30	[81]

^a All the preparations carried out in air.^b Obtained by matrix reaction method.

alloy (Inconel) container [91] closed tightly with a silver lid. Alternatively, the reactant mixture is taken in the form of a pellet, wrapped in a platinum [92] or gold [93] foil and then sealed in a quartz tube. This method has the advantage of carrying out the reaction under a vacuum. Some workers place the reactant pellet in an alumina crucible [94] which is then sealed in a quartz ampoule. Thallium-excess starting compositions have been employed by a few workers to compensate for the thallium loss during the reaction [95].

In the preparation of the thallium cuprates, the matrix reaction method is often employed. Here, a mixed oxide containing all the metal ions other than the volatile thallium oxide is first prepared by reacting the corresponding oxides and/or carbonates around 1200 K for 24 h in air [89, 96]. The freshly prepared mixed oxide is then taken with a calculated quantity of Tl_2O_3 and heated at appropriate temperatures in a sealed tube. This method is desirable when a carbonate is used as the starting material. Some of the thallium cuprates have been prepared by a modified matrix method [97] wherein a thallium-containing precursor such as $\text{Ba}_2\text{Tl}_2\text{O}_5$ is prepared first and then reacted with other components under closed conditions. Thallium-containing precursors are less volatile than Tl_2O_3 , so that the loss of thallium is minimized during the preparation.

Thermodynamic and kinetic factors associated with the synthesis of thallium cuprates are complex due to the existence of various phases which are structurally related and which can therefore intergrow with one another. In fact, one of the common defects that occurs in the thallium cuprates is the presence of random intergrowths between the various layered phases [98]. Furthermore, many of the thallium, lead and bismuth superconductors are metastable phases which are entropy stabilized [99]. The temperature of the reac-

tion, the sintering time and the starting composition are therefore all crucial to obtaining monophasic products (table 4).

The effect of the starting composition is best illustrated by the formation of the $n = 3$ phase of the bilayer thallium cuprates ($\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$). Synthesis of this compound starting from the stoichiometric mixture of the oxides corresponding to the ideal composition often yields the $n = 2$ member of the family. It was found that starting with compositions rich in Ca and/or Cu (namely $\text{TlCa}_3\text{BaCu}_3\text{O}_7$, $\text{Tl}_2\text{Ca}_4\text{Ba}_2\text{Cu}_3\text{O}_9$) yielded a nearly pure $n = 3$ phase [90, 98, 100]. The actual composition is, however, close to $\text{Tl}_{1.7}\text{Ba}_2\text{Ca}_{2.3}\text{Cu}_3\text{O}_9$. In the case of $\text{TlCaBa}_2\text{Cu}_2\text{O}_7$ (1122) starting from a stoichiometric mixture of oxides corresponding to the ideal stoichiometry always yielded a mixture of 1122 and 2122 phases, the relative proportion of the two being dependent on the conditions. It has been demonstrated recently [101] that thallium-deficient compositions corresponding to $\text{Tl}_{1-x}\text{CaBa}_2\text{Cu}_2\text{O}_7$ ($\delta = 0.0$ to 0.3) yield better monophasic 1122 materials.

The thallium content of the material not only determines the number of Tl-O layers but controls the hole concentration. As mentioned earlier, one of the good starting compositions to obtain $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ (2223) is $\text{TlCa}_3\text{BaCu}_3\text{O}_9$ (1313) which bears little relation to the composition of the final product. Another example is the formation of the $n = 4$ phase, $\text{TlCa}_3\text{Ba}_2\text{Cu}_4\text{O}_{10}$ (1324). Detailed studies [102] have shown that the 2223 phase formed initially transforms to the 1223 phase with an increase in the duration of heating. After prolonged sintering, the 1324 phase is formed at the expense of the 1223 phase. Similar transformations have also been observed in the formation process of $\text{TlCa}_4\text{Ba}_2\text{Cu}_5\text{O}_{11}$ with five Cu-O layers [103].

The Sr analogue of $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$ cannot be prepared in pure form. However, they are stabilized by

Starting composition	Conditions			Product	T_c (K)	Ref.
	Temp. (K)	Time	Gas			
$Tl_2Ba_2CuO_8$	1148	3 h	Sealed gold tubes	2201 single phase	84	[88]
$Tl_2CaBa_2Cu_2O_8$	1173	6 h	Sealed gold tubes	2122 single phase	98	[88]
	1150	3 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_4Ba_2Cu_2O_8$	1150	0.5 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_4Ca_3Ba_4Cu_5O_{10}$	1150	0.5 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_2Ba_2Cu_3O_{10}$	1173	6 h	Sealed gold tubes	2223 major phase	105	[88]
	1123	20 min	Sealed silica ampoule	2223 major phase	106	[95]
	1103	12 h				
$TlCa_3BaCu_3O_8$	1153	3 h	Sealed silica ampoules	2223 major phase	125	[100]
$Tl_2CaBa_2Cu_3O_8$	1153	3 h	Sealed silica ampoules	2223 major phase	108	[100]
$TlBa_{1.2}La_{0.8}CuO_5$	1163	3 h	Sealed silica ampoules	1021 single phase	40	[111]
$TlSrLaCuO_5$	1170	2 h	Sealed silica ampoules	1021 single phase	40	[109]
$TlSr_{2.8}Nd_{0.4}Cu_2O_8$	1170	2 h	Sealed silica ampoules	1122 major phase	80	[110]
$TlCaBa_2Cu_2O_7$	1170	3 h	Sealed silica ampoules	1122 major phase + 2122 impurity	90	[101]
$Tl_{0.5}CaBa_2Cu_2O_7$	1170	3 h	Sealed silver tubes	1122 major phase	90	[101]
$(Tl_{0.5}Pb_{0.5})CaSr_2Cu_2O_7$	1170	3 h	Sealed silica ampoules	1122 single phase	90	[104]
$Tl(Ca_{0.5}Y_{0.5})Sr_2Cu_2O_7$	1170	3 h	Sealed silver tubes	1122 single phase	90	[92]
$TlCa_2Ba_2Cu_3O_9$	1163	6 h	Sealed silica ampoules	1223 single phase	115	[94]
$(Tl_{0.5}Pb_{0.5})Ca_2Sr_2Cu_3O_9$	1198	3-12 h	Sealed gold tubes	1223 single phase	122	[105]
$Tl_{0.5}Pb_{0.5}Sr_4Cu_3O_9$	1170	2 h	Sealed silica ampoules	1223 major phase	60	[110]

partly substituting Tl by Pb (or Bi) or Ca by yttrium or a trivalent rare earth [92, 104-107]. Thus, $Tl_{0.5}Pb_{0.5}Ca_{n-1}Sr_2Cu_nO_{2n+3}$ shows a T_c of ~ 90 K for $n = 2$ and ~ 120 K for $n = 3$. $TlCa_{0.5}Y_{0.5}Sr_2Cu_2O_7$ also shows a T_c of 90 K. These cuprates in the Tl/Pb-Ca/Ln-Sr-Cu-O systems are prepared in a manner similar to the Tl-Ca-Ba-Cu-O system except that $SrCO_3$ is used in place of $BaCO_3$ or BaO_2 . $Sr_4Tl_2O_7$ has also been used as a starting material in some instances [97]. The $n = 1$ member, TlM_2CuO_5 ($M = Sr$ or Ba) is also stabilized by the substitution of Pb or Bi for Tl or a trivalent rare earth for Sr or Ba [108-111]. All these compounds showing a T_c of 40 K have been prepared by the matrix reaction method.

Single thallium layer cuprates of the general formula $Tl_{1+x}A_{2-x}Ln_2Cu_2O_9$ with $A = Sr, Ba$; $Ln = Pr$ (Nd, Ce) as well as $Tl_{0.5}Pb_{0.5}(Ln_{1-x}Ce_x)_2Sr_2Cu_2O_9$ ($Ln = Pr, Gd$) with a fluorite-type Ln_2O_3 layer have been prepared by the ceramic method [112, 113]. The as-prepared materials are semiconductors. It has been shown by Liu *et al* [114] that annealing $TlBa_2(Eu, Ce)_2Cu_2O_9$ (1222 phase) under an oxygen pressure of 100 bar induces superconductivity with a T_c of ~ 40 K.

As in the case of bismuth cuprates, the final composition of thallium cuprates is unlikely to reflect the composition of the starting mixture. Structural studies [99, 115] have shown that there is cation disorder between Tl and Ca/Sr sites. Therefore, in order to obtain a superconducting composition corresponding to a particular copper content, one has to start with various arbitrary compositions and vary the synthesis conditions. The actual composition of the final product can be quite unexpected (e.g. $Tl_{1.83}Ba_2Ca_{1.44}Cu_3O_9$ or $Tl_{1.86}Ba_{2.01}CuO_9$) as shown by analytical electron microscopy [85]. In table 4 we have listed the pre-

parative conditions employed for the synthesis of thallium cuprates by the ceramic method.

2.6. Lead cuprates

The conditions for the synthesis of superconducting lead cuprates are more stringent than for the other copper oxide superconductors. Direct synthesis of members of the $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+\delta}$ ($Ln = Y$ or rare earth) family by the reaction of the component metal oxides or carbonates in air or oxygen at temperatures below 1173 K is not possible because of the high stability of $SrPbO_3$ -related perovskite oxides. Preferential loss of the more volatile PbO leads to micro-inhomogeneities. Furthermore, Pb in these compounds is in the $2+$ state while part of the Cu is in the $1+$ state. Synthesis has therefore to be carried out under mildly reducing conditions, typically in an atmosphere of N_2 containing 1% O_2 . The most common method that has been employed for the synthesis of these lead cuprates is the matrix reaction method [116]. For $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+\delta}$ ($Ln = Y$ or rare earth), a mixed oxide containing all the metal ions except Pb is made by reacting $SrCO_3$, Ln_2O_3 or Y_2O_3 , $CaCO_3$ and CuO in the appropriate ratios around 1223 K in air for 16 h. The mixed oxide is then taken with an appropriate amount of PbO , ground thoroughly, pelletized and heated in the 1133-1198 K range in a flowing stream of nitrogen containing 1% O_2 for periods between 1 and 16 h. Generally, short reaction times and quenching the product from the sintering temperatures into liquid nitrogen in the same atmosphere gives better-quality samples. Even though this is the common method for preparing $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+\delta}$, it is not always easy to obtain samples exhibiting good, reproducible

superconducting properties. The lead cuprates from the method described above generally show broad transitions in the $R-T$ curves with negative temperature coefficients of resistance above T_c .

Studies of the dependence of T_c on the calcium concentration in the $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+x}$ system [117] have shown that heating the samples near the melting point between 1198 and 1228 K for 2 h and post-annealing in flowing nitrogen gas at a temperature between 673 and 773 K improves the superconducting properties of the samples dramatically. Direct one-step synthesis has been achieved [118] by reacting the metal oxides in sealed gold tubes around 1223 K. An alternative route to the direct synthesis from metal oxides and/or carbonates has also been demonstrated [119]. Superconductivity near 70 K has been reported in Ca-free $\text{Pb}_2\text{Sr}_2\text{LnCu}_3\text{O}_{8+x}$ ($\text{Ln} = \text{Y}$ or rare earth) employing the vacuum annealing procedure [120]. Substitution of Pb by Bi in $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+x}$ has also been carried out by the ceramic method [121]. About 30% of Pb can be substituted by Bi, and such a substitution increases the T_c up to 100 K. The $n = 0$ member of the $\text{Pb}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Ln}_x)_n\text{Cu}_{2+2n}\text{O}_{6+2n+x}$ series (namely $\text{Pb}_2(\text{SrLa})\text{Cu}_2\text{O}_{6+x}$) has been prepared successfully by this matrix reaction method [122].

Unlike the 2213-type lead cuprates, superconducting 1212-type lead cuprates of the formula $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-x}$ are synthesized in an oxidizing atmosphere. Several authors have reported direct synthesis as well as reactions under closed conditions [123–127]. In the direct synthesis of these cuprates, care is taken to prevent the loss of Pb by wrapping pellets in gold or platinum foil [127]. Rouillon *et al* [125, 126] have reported the synthesis of 1212 lead cuprates by the direct reaction of the component oxides in evacuated silica ampoules. This method has

the advantage of adjusting the oxygen partial pressure required for the synthesis. Both 2213-type and 1212-type lead cuprates have been prepared using the nitrates of the metal ions as the starting materials [128]. Although this procedure yields 2213 or 1212 phases in a single step, the product obtained always has impurities such as Y_2O_3 , CuO etc.

A superconducting lead cuprate of the formula $(\text{Pb}, \text{Cu})(\text{Eu}, \text{Ce})_2(\text{Sr}, \text{Eu})_2\text{Cu}_2\text{O}_9$ (1222 phase) containing a fluorite layer has been prepared by the direct reaction of the component metal oxides at 1273 K in oxygen atmosphere [129].

High-pressure ceramic synthesis has been employed to prepare lead cuprates of the 1212 type [130, 131]. In order to prepare $\text{Pb}_{0.5}\text{Cu}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-x}$, sintering is carried out at 1213 K for 15 h under an oxygen pressure of 100 bar followed by fast cooling to 373 K. The samples obtained from high-pressure oxygen treatment show higher T_c s than those processed at 1 bar pressure of oxygen. Substitution of Y by other rare earths has been possible by this high-oxygen-pressure method [131]. All the rare-earth substituted compounds are superconducting with T_c s in the 50–70 K range. The T_c decreases with increase in the size of the rare earth. In table 5 we summarize the conditions for the synthesis of the various lead cuprates by the ceramic method.

2.7 Electron-doped superconductors

All the cuprates discussed till now are hole superconductors. Synthesis of electron-doped cuprate superconductors of the type $\text{Ln}_{2-x}\text{M}_x\text{CuO}_{4-x}$ ($\text{Ln} = \text{Nd}, \text{Pr}, \text{Sm}, \text{Eu}$; $\text{M} = \text{Ce}, \text{Th}$), possessing the T' structure, is generally achieved by the ceramic method [132–134]. The conditions of synthesis are more stringent since the

Table 5. Conditions for the synthesis of lead cuprates by the ceramic method.

Compound	Starting materials	Conditions			Comments	T_c (K)	Ref.
		Temp. (K)	Time	Gas			
$\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+x}$	$\text{PbO} + \text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+x}$	1143	1–16 h	$\text{N}_2 + 1\% \text{O}_2$		78	[116]
	Cu_2O matrix						
	$\text{PbO}, \text{PbO}_2, \text{CaO}_2, \text{SrO}_2, \text{Y}_2\text{O}_3, \text{CuO}$	1223	12–48 h		Sealed gold tubes	78	[118]
	$\text{PbO}, \text{SrCO}_3, \text{Y}_2\text{O}_3, \text{CaCO}_3, \text{CuO}$	1073	15 h	air			
		1173	2 h	air			
$\text{Pb}_2\text{Sr}_{0.8}\text{La}_{1.2}\text{Cu}_2\text{O}_{8+x}$	$\text{PbO}, \text{La}_2\text{O}_3, \text{Sr}_2\text{CuO}_3, \text{CuO}$	1073	1–5 h	N_2		78	[119]
	$\text{PbO}, \text{SrCO}_3, \text{La}_2\text{O}_3, \text{CuO}$	1073	8 h	N_2	2202 major phase + $\text{Pb}_2\text{LaCu}_{0.5}\text{O}_3$ impurity	28	[122]
		1083					
$(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{SrLaCuO}_4$	$\text{PbO}, \text{SrCO}_3, \text{La}_2\text{O}_3, \text{CuO}$	1073	5 h	air			
		1273	2 h	O_2		25	[123]
		1123	10 h	air			
$(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-x}$	$\text{PbO}, \text{SrCO}_3, \text{Y}_2\text{O}_3, \text{CaCO}_3, \text{CuO}$	1123	1 h	O_2	1212 major phase + $\text{Sr}_2\text{Pb}_3\text{CuO}_{12}$ impurity	50	[124]
		1243	3 h	O_2	1212 major phase + $\text{Sr}_2\text{Pb}_3\text{CuO}_{12}$ impurity	47	[127]
	$\text{PbO} + \text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-x}$ matrix						
$(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-x}$	$\text{PbO}, \text{PbO}_2, \text{Sr}_2\text{CuO}_3, \text{Y}_2\text{O}_3, \text{CaO}_2, \text{Cu}_2\text{O}, \text{CuO}$	1108–1223	1–10 h		Evacuated silica tubes	100	[125]
	$\text{PbO}_2, \text{PbO}, \text{SrO}_2, \text{SrCuO}_2, \text{Y}_2\text{O}_3, \text{CaO}, \text{CuO}$	1108–1223	1–10 h		Evacuated silica tubes	80	[126]
$(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1.75}\text{Eu}_{0.25})\text{Cu}_2\text{O}_8$	$\text{PbO}, \text{SrCO}_3, \text{Eu}_2\text{O}_3, \text{CeO}_2, \text{CuO}$	1123	10 h	air	Single phase	25	[129]
		1323	1 h	O_2	1222		

material, by making sure that extra electron donated by Ce^{4+} or Th^{4+} does not increase the oxygen content of the cuprate. For this reason, samples after calcination and sintering at 1323 K in air (for 24 h) are annealed in a reducing atmosphere (typically Ar, N_2 or dilute H_2) at 1173 K to achieve superconductivity. Samples prepared in this manner show a negative temperature coefficient of resistance above T_c in the R - T curves; the resistivity drop at T_c is also not sharp. An alternative synthetic route involves the reaction of pre-reacted $\text{NdCeO}_{3.5}$ material with the required amounts of Nd_2O_3 and CuO at 1253 K for a minimum period of 48 h in flowing oxygen [135]. The samples are then rapidly quenched from 1253 K in an argon atmosphere to achieve superconductivity. This procedure eliminates the slow diffusion of Ce throughout the $\text{Nd}_2\text{CuO}_{4-x}$ host and gives uniform concentrations of cerium and oxygen. Samples obtained from this route show a sharp transition at 21 K.

Superconductivity with a T_c of 25 K is induced by doping fluorine for oxygen in Nd_2CuO_4 . This has been accomplished by taking NdF_3 as one of the initial reactants [136]. Substitution of either Ga or In for copper in non-superconducting $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-x}$ also induces superconductivity [137, 138].

2.8. Infinite-layer cuprates

Discovery of superconductivity in cuprates containing infinite CuO_2 layers has been of great importance in understanding the phenomenon. Very high pressures have been employed for obtaining the infinite-layer cuprates. Both hole-doped (e.g. $\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$) and electron-doped ($\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$) infinite-layer cuprate superconductors with a maximum T_c of 110 K have been reported [139–142]. Infinite-layered cuprates of the type $(\text{Ba}, \text{Sr})\text{CuO}_2$, $(\text{Ca}, \text{Sr})\text{CuO}_2$ are synthesized in an oxidizing atmosphere under high hydrostatic pressure [139, 140, 142]. Electron-doped $\text{Sr}_{0.86}\text{Nd}_{0.14}\text{CuO}_2$ is also prepared under high hydrostatic pressures [141]. Metal nitrates are generally used as the starting materials since carbonates of Ba, Sr and Ca have high decomposition temperatures. After decomposing the metal nitrates at around 873–1123 K in air, the product is subjected to high pressure to obtain the superconducting phases. $\text{Sr}_{0.86}\text{Nd}_{0.14}\text{CuO}_2$, which superconducts at 40 K, is made under a hydrostatic pressure of 25 kbar at 1273 K. Superconducting $(\text{Ca}, \text{Sr})\text{CuO}_2$ is prepared at 1273 K under 6 GPa pressure. Deficiency of Sr and Ca as well as the oxidizing atmosphere make this phase superconducting, and the oxidizing atmosphere is provided by heating a capsule containing KClO_4 along with the sample. This cuprate has a T_c (onset) of 110 K.

3. Coprecipitation and precursor methods

Coprecipitation involves the separation of a solid containing various ionic species chemically bound to one

neous coprecipitation process can result in the formation of crystalline or amorphous solids. Coprecipitation of well defined stoichiometry with respect to the metal ions is obtained only when the following conditions are satisfied.

(i) The precipitating agent is a multivalent organic compound which can coordinate with more than one metal ion, and the precipitation rate is fast.

(ii) The solid precipitating out of the solution should be really insoluble in the mother liquor.

The anions generally preferred for coprecipitation of oxidic materials are carbonates, oxalates, citrates etc. The same is true of high- T_c cuprates. The precipitates in some instances could be genuine precursors or solid solutions [5, 6]. It is well known that precursor solid solutions drastically bring down diffusion distances for the cations and facilitate reactions in the solid state. We shall not distinguish precursor solid solutions precipitated from solutions from other precursors in this discussion.

The precipitates (carbonate, oxalate etc) are heated at appropriate temperatures in a suitable atmosphere to obtain the desired cuprate. Some of the advantages of the coprecipitation technique over the ceramic method are an homogeneous distribution of components, a decrease in the reaction temperatures and of the duration of annealing, a higher density and a lower particle size of the final product. The major drawback of this route is the control over the stoichiometry of the final product.

3.1. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

La, Sr and Cu in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ are readily coprecipitated as carbonates [11, 12, 143]. For this purpose the required quantities of the various metal nitrates are dissolved together in distilled water. Alternatively, the corresponding oxides are dissolved in nitric acid to give a nitrate solution and the pH of the solution is adjusted to 7–8 by the addition of KOH solution. A solution of K_2CO_3 of appropriate strength is then slowly added under stirring to give a light blue precipitate which is thoroughly washed. The precipitate is dried at 420 K and calcined at 1070 K for 8 h in air. The resulting black powder is ground and pelletized and sintered at 1270 K for 16 h in air to obtain monophasic $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, superconducting at 35 K.

Instead of as carbonate, the metal ions are also readily precipitated as oxalate by the addition of either oxalic acid or potassium oxalate to the solution of metal nitrates [11, 12, 144, 145]. The precipitated oxalate is then decomposed to obtain the cuprate. This method has certain disadvantages:

(i) La^{3+} in the presence of an alkali metal oxalate first yields lanthanum oxalate which further reacts with the precipitating agent to give a double salt. Control of stoichiometry therefore becomes difficult, leading to multiphasic products.

(ii) The relative solubilities of some of the oxalates also pose difficulties. For example, SrC_2O_4 is nearly four times more soluble than SrCO_3 .

3.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$

$\text{YBa}_2\text{Cu}_3\text{O}_7$ and related 123 compounds can be obtained via coprecipitation of the component metals (from a nitrate solution) as a formate [146, 147], acetate [148], oxalate [12, 149–156], hyponitrite [157] or hydroxycarbonate [158, 159]. Some of these precipitates could be genuine precursor compounds as is indeed the case with the hyponitrite.

In oxalate coprecipitation [12, 149–152], oxalic acid solution of appropriate concentration is added to an aqueous solution of mixture of nitrates of Y, Ba and Cu and the pH of the solution is adjusted to 7.5 (by dilute NH_3). The pale green slurry thus formed is digested for 1 h, filtered and dried. The oxalate is converted to orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by heating at 1053 K in air for 5 days followed by oxygenation at 723 K. This procedure, even though successful in making superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in small particulate form, often results in undesirable stoichiometry because of the moderate solubility of barium oxalate. Furthermore, rare-earth ions in the presence of ammonium oxalate give a double salt with the excess oxalate which competes with the precipitation of copper and barium oxalates. These difficulties can be overcome either by taking a known excess (wt%) of barium and copper or by using triethylammonium oxalate as the precipitant in aqueous ethanol medium [153–155]. The alcoholic medium decreases the solubility of barium oxalate and the pH of the solution is controlled *in situ*.

A better method of homogeneous coprecipitation of oxalates is that of Liu *et al* [156] using urea and oxalic acid. Urea, on heating, is hydrolysed liberating CO_2 and NH_3 , and thus gradually adjusting the pH throughout the solution. The CO_2 liberated controls the bumping of the solution during digestion. The oxalate coprecipitation route is widely described in the literature. The reactive powders obtained by the oxalate coprecipitation method decrease the sintering temperature. The formation of BaCO_3 in the intermediate calcining step makes it difficult to obtain $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in pure form.

Complete avoidance of the formation of BaCO_3 during the synthesis is possible using the hyponitrite precursor [157]. The hyponitrite precursor is obtained from a nitrate solution of Y, Ba and Cu ions by the addition of an aqueous $\text{Na}_2\text{N}_2\text{O}_2$ solution. The precipitate is converted into superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by heating at around 973 K in an argon atmosphere, followed by oxygen annealing at 673 K. Although this route provides a convenient means of obtaining the 123 cuprate at much lower temperatures than with other methods, there is a possibility of contamination of alkali metal ions during the course of the precipitation.

$\text{YBa}_2\text{Cu}_3\text{O}_7$ can also be prepared by the hydroxycarbonate method [158, 159]. Here, KOH and K_2CO_3

are employed to precipitate copper as the hydroxide and Y and Ba as the carbonates in the pH range of 7–8. By employing NaOH and Na_2CO_3 , complete precipitation as hydroxycarbonate is attained at a pH of ~13. The product from the above two procedures is homogeneous, showing sharp onset of superconductivity at 92 K. The possibility of contamination by alkali metal ions cannot, however, be avoided.

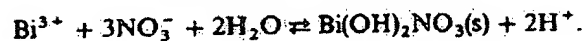
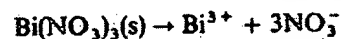
3.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$

$\text{YBa}_2\text{Cu}_4\text{O}_8$ can be prepared by the oxalate route [160] wherein the solution of Y, Ba and Cu nitrates in water is added dropwise into oxalic acid–triethylamine solution under stirring. Complete precipitation of Y, Ba and Cu with the desired stoichiometry of 1:2:4 is achieved in the pH range of 9.3–11.3. The precipitated oxalates are filtered and dried in air at 393 K. The solid obtained is then heated in the form of pellets at 1078 K in flowing oxygen for 2–4 days. The product after quenching in air shows the 124 phase as the major product with a T_c of 79 K.

An alternative coprecipitation route for the synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ is the method of Chen *et al* [161] in which the aqueous nitrate solution of the constituent metal ions is mixed with 8-hydroxyquinoline–triethylamine solution. The precipitated oxine is filtered, washed, dried and sintered at 1088 K in oxygen for 3 days to yield phase-pure $\text{YBa}_2\text{Cu}_4\text{O}_8$ showing a T_c of 80 K. Ethylenediaminetetraacetic acid [161] as well as carbonate routes [162] have also been employed for the preparation of $\text{YBa}_2\text{Cu}_4\text{O}_8$. Coprecipitation using triethylammonium oxalate has been exploited for substituting Sr in place of Ba in $\text{YBa}_2\text{Cu}_4\text{O}_8$ [163].

3.4. Bismuth cuprates

Very few coprecipitation studies have been carried out on the preparation of bismuth cuprates. One reason may be that despite the good sample homogeneity generally obtained through solution methods, the chemistry of bismuth cuprates is rather complex. It is not that easy to find compounds of all the constituent metal ions soluble in a common solvent; controlling the stoichiometry in these cuprates is also difficult in the coprecipitation procedure. Furthermore, bismuth nitrate, which is often used as one of the starting materials, decomposes in cold water to a basic nitrate precipitate as given by



This problem can be overcome to some extent by preparing the nitrate solution of bismuth in nitric acid or by starting with bismuth acetate instead of the nitrate.

Bidentate ligands such as the oxalate are found to react more rapidly than multidentate ligands such as citric acid [164–174] in the coprecipitation process. Complexes of oxalic acid are also more stable than

the stoichiometry because of the relative solubility of BiC_2O_4 or SrC_2O_4 .

A straightforward oxalate coprecipitation is achieved by dissolving the acetates of Bi, Ca, Sr and Cu in glacial acetic acid and then adding excess oxalic acid to the solution [164]. The oxalate precipitate is dried and decomposed at around 1073 K in air and processed in the 1103–1123 K range for periods ranging from 24 h to 4 days, depending on the starting composition. The $n = 2$ (2122) member obtained by this procedure shows zero resistance at 83 K. In another procedure reported by Zhang *et al* [165], first the Sr/Ca/Cu nitrate solutions are mixed in the required molar ratio. Into this solution is poured a solution of bismuth nitrate prepared in nitric acid along with oxalic acid. The complete precipitation occurs at a pH of around 5 (attained by the addition of aqueous NaOH). This process involves the possibility of contamination of sodium ions; this has been circumvented by using $\text{N}(\text{CH}_3)_4\text{OH}$ to adjust the pH of the solution [166] and complete precipitation of the oxalates occurs at a pH of 12. All these procedures, however, produce mixed-phase samples.

For the preparation of the monophasic lead-doped $n = 3$ member (2223), oxalate coprecipitation has been found effective [167–174]. In the procedure reported by Chiang *et al* [171], the molar ratio of the chelating agent (oxalic acid) and the nitrate anions (from the metal nitrate solutions) is fixed at 0.5 and the pH, adjusted by NH_4OH solution, at which complete precipitation occurs is 6.7. The product from this method, $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7$, after sintering at 1133 K in air for 72 h, shows a T_c of 110 K.

Coprecipitation as oxalates to prepare the lead-doped $n = 3$ member (2223) has been achieved from an ethylene glycol medium using triethylammonium oxalate and oxalic acid [172]. A more easily controlled and reproducible oxalate coprecipitation procedure appears to be that of Shei *et al* [173] where in a mixture of triethylamine and oxalic acid is employed. The advantage of using triethylamine is that it has a higher basicity and a lower complexing ability towards Cu(II) than has ammonia. Control of the stoichiometry of the final product is therefore better obtained with this procedure; precipitation occurs in the pH range 1.5–2.2. The coprecipitated oxalates sintered at 1133 K in air for a minimum period of 72 h give monophasic $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ with a T_c of 110 K. It is possible to avoid adjusting the pH in the coprecipitation of oxalates [174]. The procedure involves coprecipitating the oxalates from dilute acetate solutions instead of from nitrate solutions. The oxalates are then converted to nearly phase-pure $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (T_c of 106 K) by sintering at 1123 K in air for 160 h.

Carbonate coprecipitation has also been carried out for the synthesis of superconducting bismuth cuprates [175, 176], but the method does not yield monophasic products.

Coprecipitation of $n = 3$ in-phase cuprates from aqueous solutions as oxalates is hindered by the solubility of thallium oxalate. However, Bernhard and Gritzner [177] have found that complete coprecipitation as oxalates can be achieved by starting with thallium acetate in glacial acetic acid medium. In the procedure reported for the preparation of the $n = 3$ member (2223), stoichiometric amounts of thallium acetate, CaCO_3 , BaCO_3 and copper acetate are dissolved in water containing glacial acetic acid. The solution containing all the cations is then added to a solution of oxalic acid (excess) under stirring. The precipitate, after digestion for 1 h, is filtered, washed and dried. The oxalates are heated in the form of pellets (wrapped in gold foil) at around 1173 K for 6 min in an oxygen atmosphere. The product after annealing in the same atmosphere shows 2223 as the major phase with a T_c of 118 K.

3.6. Lead cuprates

Carbonate coprecipitation is found to be satisfactory for the synthesis of representative members of superconducting lead cuprates [128] of 2213 and 1212 types, namely $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+0}$ and $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-0}$. Coprecipitation as carbonates has been achieved by adding the nitrate solution of the constituent metal ions to an aqueous solution of sodium carbonate (in excess) under constant stirring. The carbonate precipitate thus obtained is washed and dried. The decomposed powder is heated in the form of pellets around 1153 K in a suitable atmosphere. $\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+0}$ obtained by this method after heating for 4 h in nitrogen containing 1% O_2 showed 2213 as the major phase ($T_c \sim 74$ K) with impurities such as Y_2O_3 , CuO . The 1212 phase obtained after heating in oxygen at 1153 K for 12 h showed a broad transition with a T_c (onset) of 100 K. This method has the advantage of single heating rather than the multistep procedures required in the other methods.

4. Sol-gel process

The sol-gel process is employed in order to get homogeneous mixing of cations on an atomic scale so that the solid state reaction occurs to completion in a short time and at the lowest possible temperature. The term sol often refers to a suspension or dispersion of discrete colloidal particles, while a gel represents a colloidal or polymeric solid containing a fluid component which has the internal network structure wherein both the solid and the fluid components are highly dispersed. In the sol-gel process a concentrated sol of the reactant oxides or hydroxides is converted to a semi-rigid gel by removing the solvent. The dry gel is heated at an appropriate

temperature to obtain the product. Most of the reactions in the sol-gel process occur via hydrolysis and polycondensation.

Two different routes for the sol-gel process are usually described in the literature for the synthesis of high- T_c cuprate superconductors:

- (i) Via molecular precursors (e.g. metal alkoxides) in organic medium;
- (ii) Via ionic precursors in aqueous medium (citrate gel process).

The purity, microstructure and physical properties of the product are controlled by varying the precursor, solvent, pH, firing temperatures and atmosphere of heat treatment.

4.1. 214 Cuprates

Superconducting 214 compounds are prepared both by means of organometallic precursor [178] and by the citrate gel process [11]. Lanthanum 2,4-pentanedionate, barium 2,4-pentanedionate and copper (II) ethyl hexanoate are mixed at room temperature in the appropriate ratios in methoxyethanol medium to obtain the organometallic precursor. After vigorous stirring at room temperature, the precursor gel is converted to monophasic $\text{La}_{1.5}\text{Ba}_{0.5}\text{CuO}_4$ (T_c 23 K) by firing at 873 K in oxygen.

In the citrate gel process, a mixture of citric acid and ethylene glycol is added to the solution containing the required quantities of metal nitrates. The resulting solution is vigorously stirred and heated around 393 K. During this process, oxides of nitrogen evolve, resulting in a viscous gel. The gel is decomposed at 673 K in air and the resulting black powder is then given the necessary heat treatment to obtain the superconducting oxide.

4.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$

In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the alkoxide precursors are both very expensive and difficult to obtain. In addition, the solubility of copper alkoxides is very low in organic solvents and yttrium alkoxides are readily hydrolysed even by a trace of water. Despite these difficulties, superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has been prepared using alkoxides [157, 179–181]. A simple reaction involving $\text{Y}(\text{OCHMe}_2)_3$, $\text{Ba}(\text{OCHMe}_2)_2$ and $\text{Cu}(\text{NBu}_2)_2$ in THF in an argon atmosphere gives the organometallic precursor [157]. The precursor powder, after removal of the solvent, is sintered at 973 K in flowing argon to obtain tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Following oxygenation at 673 K, the product shows a T_c of 85 K. Superconducting properties have been improved by using *n*-butoxides of Y, Ba and Cu in butanol solvent [179].

Alternatively, methoxyethoxides of yttrium, barium and copper have been used as precursors in methoxyethanol–methyl ethyl ketone–toluene solvent mixture to prepare $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [180]. In some of the preparations, $\text{Cu}(\text{NO}_3)_2$ (soluble in ethanol) or copper

acetylacetonate (soluble in toluene) is used along with the alkoxides of yttrium and barium to overcome the problem of low solubility of copper alkoxides [182, 183]. Organometallic precursors involving propionates [153] and neodeconates [184] have also been used for preparing $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Modified sol-gel methods which do not involve the metal alkoxide precursors have been employed by many workers. Thus, Nagano and Greenblatt [185] have employed metal nitrates dissolved in ethylene glycol. After refluxing around 353 K under vigorous stirring, a bluish green colloidal gel is obtained. The gel is converted into orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by heating to 1223 K in flowing oxygen. Precipitating all the three ions as hydroxides also results in fine colloidal particles of the starting materials [186–188]. The precipitation is generally carried out by the addition of NH_4OH [186], $\text{N}(\text{CH}_3)_4\text{OH}$ [187] or $\text{Ba}(\text{OH})_2$ [188] to a solution of metal nitrates (pH range 7–8). These hydroxides are decomposed around 1223 K in oxygen to give $\text{YBa}_2\text{Cu}_3\text{O}_7$ showing a T_c of 93 K.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has been prepared by the citrate gel process [189–193]. In this method 1 g equivalent of citric acid is added to each gram equivalent of the metal. The pH of the solution is adjusted to around 6 (either by NH_4OH or by ethylenediamine). Evaporation of the solvent (water) around 353 K, results in a viscous dark blue gel. The gel is decomposed and the powder sintered in the form of pellets at 1173 K in oxygen to obtain orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($T_c = 93$ K). By this method, ultrafine homogeneous powders (particle size $\sim 0.3 \mu\text{m}$) are obtained. The crucial step in this process is the adjustment of the pH which controls the stoichiometry of the final product. This limitation has been overcome by dispersing the citrate metal ion complexes in a solvent mixture of ethylene glycol and water [194, 195].

Problems such as the formation of BaCO_3 during the calcination step, filtration and contamination of alkali metal ions in the final product are avoided in the sol-gel process. Furthermore, perfect homogeneity is obtained before calcination. The sol-gel process (e.g. citrate process) has the advantage over the other methods in that the gel can be used for making thick and thin superconducting films, fibres etc which have technological importance [179, 185, 186, 196–198].

4.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$

The sol-gel method offers a good alternative to the ceramic method for the synthesis of superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$. The following procedure has been used to prepare $\text{YBa}_2\text{Cu}_4\text{O}_8$ at 1 atm oxygen pressure [199]. Appropriate quantities of $\text{Y}(\text{n-OC}_2\text{H}_5)_3$, $\text{Ba}(\text{s-OC}_2\text{H}_5)_2$ and $\text{Cu}(\text{s-OBu})_2$ in butanol–xylene mixture are refluxed in an argon atmosphere at 343 K for a period of 30 h. The fine powder after the vigorous reaction is freed from the solvent and dried. The powder is heated in the form of pellets at 1033 K in flowing oxygen to obtain superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$.

used as the source of copper in this procedure [200].

In the modified citrate gel process to prepare $\text{YBa}_2\text{Cu}_3\text{O}_8$ [201, 202], 1 g equivalent of citric acid is added for each gram equivalent of the metal and the pH of the solution is adjusted to ~ 5.5 by the addition of ethylenediamine. The resulting clear solution is evaporated to yield a viscous purple gel. The decomposed gel is sintered in flowing oxygen for 3–5 days at 1088 K to obtain nearly monophasic $\text{YBa}_2\text{Cu}_3\text{O}_8$ ($T_c = 66$ K). Kakihana *et al* [203] have reported the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_8$ using a precursor obtained from citrate metal ion complexes uniformly dispersed in a solvent mixture of ethylene glycol and water. This method yields phase-pure $\text{YBa}_2\text{Cu}_3\text{O}_8$ ($T_c \sim 79$ K) and eliminates the need to adjust the pH.

4.4. Bismuth cuprates

There have been very few reports of the preparation of bismuth-based cuprate superconductors by the alkoxy sol-gel method [204]. Some of the difficulties arise because the relevant bismuth/lead alkoxides are not readily available; it is also not easy to get a common organic solvent to dissolve the various metal alkoxides simultaneously. Dhalle *et al* [204] have, however, attempted to synthesize the lead-doped $n = 3$ member (2223) using organometallic precursors involving propionates. The starting materials were taken in the form of nitrates and converted into propionates by the addition of an excess of 100% propyl alcohol. This step was followed by the addition of ammonium hydroxide and ethylene glycol to increase the alkoxy anion concentration, thus in turn increasing the viscosity of the solution. All the solutions were mixed together and dried at 353 K. The resin after calcination at 1123 K in air and sintering at 1118 K gave a mixture of the $n = 3$ and $n = 2$ members.

A simple sol-gel method involving the addition of dilute ammonia to an aqueous solution containing nitrates of Bi, Sr and acetates of Ca, Cu and Pb (until the pH of the solution reached around 5.5) has also been employed to prepare bismuth cuprates [205, 206]. The blue solution after concentrating at around 343 K gives a viscous gel. The gel is decomposed and the powder sintered at around 1128 K in air. The product from this procedure is multiphasic showing a T_c of 104 K. The simplicity of the method and the formation of the $n = 3$ phase in a short time makes it somewhat superior to the conventional ceramic route. The modified citrate gel process has been employed to prepare the $n = 2$ member (2212) in pure form with a T_c of 78 K [193].

4.5. Lead cuprates

The modified citrate gel process has been successfully employed by Mahesh *et al* [207] for the synthesis of lead cuprates of the 2213 or 1212 type. In a typical procedure, a mixture of citric acid and ethylene glycol in

is concentrated at 373 K in order to get a viscous gel. The gel after decomposition is heated in the form of pellets in the temperature range of 1073–1173 K either in N_2 containing 1% O_2 or in an oxygen atmosphere. $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+\delta}$ obtained from this process shows a sharp superconducting transition at 70 K. The 1212 cuprate also shows a sharp transition at 60 K. This process is superior to the ceramic procedure for synthesizing superconducting lead cuprates.

5. Alkali flux method

Strong alkaline media, either in the form of solid carbonate fluxes, molten hydroxides or highly concentrated alkali solutions can be employed for the synthesis of high- T_c cuprate superconductors. The alkali flux method takes advantage of both the moderate temperatures of the molten media (453–673 K) as well as of the acid-base characteristics of molten hydroxides to simultaneously precipitate oxides or oxide precursors such as hydroxides or peroxides of the constituent metals. The method stabilizes higher oxidation states of the metal by providing an oxidizing atmosphere.

Employing fused alkali hydroxides, Ham *et al* [208] have synthesized superconducting $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{K}$ or Na or vacancy) at relatively low temperatures (470–570 K). In this method, stoichiometric quantities of La_2O_3 and CuO are added to a molten mixture containing KOH and NaOH (in an approximately 1:1 ratio) in a Teflon crucible and heated at around 570 K in air for 100 h. The 1:1 mixture of KOH and NaOH melts at 440 K and since the alkali hydroxides generally contain some water, the melt is acidic and can readily dissolve oxides such as La_2O_3 and CuO . The black crystals obtained from the reaction (after washing away the excess hydroxide with water) show a T_c of 35 K. Since the reaction is carried out in alkali hydroxides, incorporation of Na^+ or K^+ ions for La^{3+} in the lattice of La_2CuO_4 cannot be ruled out. It should be noted that superconducting alkali-doped La_2CuO_4 is normally prepared at higher temperatures in sealed gold tubes [209]. Recently, alkaline hypobromite oxidation has been employed to obtain $\text{La}_2\text{CuO}_{4+\delta}$ with a T_c of 44 K [210].

Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c \sim 88$ K) has also been prepared using the fused eutectic of sodium and potassium hydroxides in a similar manner to that described above [211]. The problem of contamination of alkali metals in the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ has been overcome by using the $\text{Ba}(\text{OH})_2$ flux [211]. The procedure involves heating a mixture containing stoichiometric amounts of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{OH})_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in an open ceramic crucible at around 1023 K in air for a short time (about 10 min) and then slowly cooling the melt to room temperature. Since $\text{Ba}(\text{OH})_2$ has two hydration states, one melting at 351 K and the other at 681 K, the lower-melting hydrate acts as the solvent for the nitrates of copper

and yttrium while the high-melting hydrate serves as the medium for intimate mixing of the reactants. The precipitate obtained from the melt, after washing with water, is sintered in air at around 1173 K followed by oxygenation at 773 K. This method yields an orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase (with little CuO impurity) showing a T_c of 92 K.

The flux method eliminates the need for mechanical grinding and introduction of carbon-containing anions, which is often encountered in the solution routes. Furthermore, the method is efficient and cost-effective.

6. Combustion method

Although many of the solution routes discussed earlier yield homogeneous products, the processes involved are quite complex. Combustion synthesis or self-propagating high-temperature synthesis (SHS), first developed by Merzhanov and Borovinskaya [212], provides a simple and rapid means of preparing inorganic materials, many of which are technologically important. Combustion synthesis is based on the principle that the heat energy liberated by many exothermic non-catalytic solid-solid or solid-gas reactions can self-propagate throughout the sample at a certain rate. This process can therefore occur in a narrow zone which separates the starting substances and reaction products.

Self-propagating combustion has been employed recently in this laboratory to synthesize members of almost all families of cuprate superconductors (except for the thallium cuprates) [213]. The method involves the addition of an appropriate fuel to a solution containing the metal nitrates in the proper stoichiometry. The ratio of the metal nitrates to the fuel is such that when the solution is dried at around 423 K, the solid residue undergoes flash combustion, giving an ash containing the mixture of oxides in the form of very fine particles (particle size 0.3–0.5 μm). The ash is then given proper heat treatment under the desired atmosphere to obtain the cuprate. The small particle size of the ash facilitates the reaction between the metal oxides due to smaller diffusion distances between the cations. Fuels such as urea [213, 214], glycine [213, 215] and tetraformal triazine (TFTA) [216] are generally employed for synthesizing cuprate superconductors. Ultrafine particles of copper metal can also act as an internal fuel wherein the combustion is initiated by flashing a laser beam for a short time [217]. Some of the cuprate superconductors which have been prepared [213] by this route include $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($T_c = 35$ K), $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c = 90$ K), $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c = 80$ K), $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ ($T_c = 85$ K), $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$ ($T_c = 60$ K) and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ ($T_c \sim 30$ K).

7. Other methods

In addition to the various synthetic methods discussed hitherto, a few other methods such as spray drying [218–221], freeze drying [186, 222, 223], use of metallic precursors [224, 225] and electrochemical methods

[226, 227] have also been employed for the preparation of cuprate superconductors in bulk form. In spray drying, a solution containing the metallic constituents, usually in the form of nitrates, is sprayed in the form of fine droplets into a hot chamber. The solvent evaporates instantaneously, leaving behind an intimate mixture of the reactants which on heating at the desired temperature in a suitable atmosphere yields the cuprate. Some of the superconducting cuprates prepared by this method include $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c = 91$ K) [218], $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c = 81$ K) [219] and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($T_c = 101$ K) [220, 221]. In freeze drying, the reactants (in a common solvent) are frozen by immersing in liquid nitrogen. The solvent is removed at low pressures to obtain the initial reactants in fine powder form, and these are then processed at an appropriate temperature. For example, $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c = 87$ K) [186], $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c = 79$ K) [222] and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_7$ ($T_c = 101$ K) [223] have been prepared by this method.

Metallic precursors have been used in the preparation of 123 and 247 cuprates [224, 225]. For example, oxidizing an Er–Ba–Cu alloy around 1170 K gives superconducting $\text{ErBa}_2\text{Cu}_3\text{O}_7$ with a T_c of 87 K [224]. Similarly $\text{Yb}_2\text{Ba}_4\text{Cu}_8\text{O}_{13}$ has been obtained by heating an alloy composition of YbBa_2Cu_3 (with 33 wt% of silver) under 1 atm oxygen at 1173 K [225].

Making use of electrochemical oxidation, $\text{La}_2\text{CuO}_{4+x}$ with a T_c of 44 K has been prepared at room temperature, which is otherwise possible only by use of high oxygen pressures [226, 227].

8. Oxygen non-stoichiometry

Oxygen stoichiometry plays a crucial role in determining the superconducting properties of many of the cuprates. Thus, stoichiometric La_2CuO_4 is an insulator, while an oxygen-excess material prepared under high oxygen pressures shows superconductivity with a T_c of 35 K [15]. The same holds for the next member of the homologous family, $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$ which is superconducting only when there is an oxygen excess [17]. The excess oxygen donates holes in these two systems. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, oxygen can be easily removed giving rise to tetragonal non-superconducting $\text{YBa}_2\text{Cu}_3\text{O}_6$. The $\text{YBa}_2\text{Cu}_3\text{O}_6$ material can be prepared by heating $\text{YBa}_2\text{Cu}_3\text{O}_7$ in an argon atmosphere at 973 K for extended periods of time [228]. The variation of T_c with oxygen stoichiometry, δ , is well known [229, 230]. When δ reaches 0.5, there is an intergrowth of $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$, and at this composition, the material shows a T_c of 45 K. The $\delta = 0.5$ composition is obtained by quenching $\delta \approx 0$ material, heated in a nitrogen atmosphere at 743 K [231]. Similarly, by quenching $\text{YBa}_2\text{Cu}_3\text{O}_7$ at 783 K in air, $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ (showing a T_c of ~ 60 K) is prepared [231]. The T_c of 90 K is found only when $\delta \leq 0.2$. $\text{YBa}_2\text{Cu}_3\text{O}_6$ is readily oxidized back to $\text{YBa}_2\text{Cu}_3\text{O}_7$. It may be noted that this oxidation–reduction process in

Cuprate	T_c (approx.)	Methods of synthesis ^a
$\text{La}_{2-x}\text{Sr}_x(\text{Ba})\text{CuO}_4$	35	Ceramic*, sol-gel, combustion, coprecipitation
$\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_8$	60	Ceramic (high O_2 pressure)*
$\text{La}_2\text{CuO}_{4+\delta}$	40	Ceramic (high O_2 pressure)* alkali-flux, hypobromite*
$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	90	Ceramic (annealing in O_2)*, sol-gel*, coprecipitation*, combustion
$\text{YBa}_2\text{Cu}_4\text{O}_8$	80	Ceramic (high O_2 pressure), ceramic (with Na_2O_2)* sol-gel*, coprecipitation*
$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	90	Ceramic (air-quench)* sol-gel*, combustion, melt (glass) route*
$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$	110	Ceramic*, sol-gel, melt route
$\text{TiCaBa}_2\text{Cu}_2\text{O}_{8+\delta}$	90	Ceramic (sealed Ag/Au tube)*
$\text{TiCa}_2\text{Ba}_2\text{Cu}_3\text{O}_{8+\delta}$	115	Ceramic (sealed Ag/Au tube)*
$\text{Ti}_2\text{Ba}_2\text{CuO}_6$	90	Ceramic (sealed Ag/Au tube)*
$\text{Ti}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	110	Ceramic (sealed Ag/Au tube)*
$\text{Ti}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$	125	Ceramic (sealed Ag/Au tube)*
$\text{Ti}_{0.5}\text{Pb}_{0.5}\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$	90	Ceramic (sealed Ag/Au tube)*
$\text{Pb}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$	70	Ceramic (low O_2 partial pressure)*, sol-gel* (low O_2 partial pressure)
$\text{Pb}_{0.5}\text{Cu}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	45	Ceramic (flowing O_2)*
$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	30	Ceramic (low O_2 partial pressure)*
		Coprecipitation (low O_2 partial pressure)*
$\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	40–110	Ceramic (high pressures)*
$\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	40–110	Ceramic (high pressures)*

* Recommended methods are indicated by asterisks.

^b Other rare-earth compounds of this type are also prepared by similar methods. Oxygen annealing is done below the orthorhombic-tetragonal transition.

^c Sr analogues of these compounds with different substitutions at Ca and Ti sites are prepared by a similar procedure.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is of topochemical character. The other analogous rare-earth 123 cuprates also behave in a similar way with respect to the variation of δ with T_c [232].

While $\text{YBa}_2\text{Cu}_4\text{O}_8$ has high oxygen stability, $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{13-\delta}$ shows a wide range of oxygen stoichiometry ($0 \leq \delta \leq 1$) [233]. The maximum T_c of 90 K is achieved when δ is close to zero, and when δ reaches unity the material shows a T_c of 30 K; there is no structural phase transition accompanying the variation in oxygen stoichiometry. Usually, both yttrium 124 and 247 cuprates and their rare-earth analogues, prepared by the ceramic method under 1 atm oxygen pressure, show δ close to zero.

Bismuth cuprates of the type $\text{Bi}_2(\text{Ca}, \text{Sr})_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ are best prepared by quenching the samples in air or by annealing in a nitrogen atmosphere at appropriate temperatures [53, 234]. Heating the samples in an oxygen atmosphere is no good, possibly because the extra oxygen may add on to the Bi-O layers. In the case of the lead-doped $n = 3$ member (2223), preparing the samples under low partial pressures of oxygen is found to increase the volume fraction of the superconducting phase [235, 236]. The $n = 1$ member, $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, shows metallic behaviour when there is excess oxygen [237]. By annealing in a reducing atmosphere (Ar or N_2), the excess oxygen can be removed to induce superconductivity.

Oxygen stoichiometry has a dramatic influence on the superconducting properties of thallium cuprates [94, 108, 109, 238–246]. For example, thallium cuprates of the $\text{TiCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$ family, derivatives of the

$\text{TiCa}_{n-1}\text{Sr}_2\text{Cu}_n\text{O}_{2n+3}$ family and $\text{Ti}_2\text{Ba}_2\text{CuO}_6$ often have excess oxygen when prepared in sealed tubes. By annealing these samples in a reducing atmosphere (Ar , dilute H_2 , N_2 or vacuum) at appropriate temperatures, the excess oxygen is removed to induce superconductivity in some cases [108, 109, 238]. Annealing at low oxygen partial pressures or in a reducing atmosphere also increases the T_c of some of the superconducting thallium cuprates to higher values by decreasing the oxygen content [94, 239–246]. These variations are clearly related to the hole concentration where the number of holes decreases by removing excess oxygen, thereby giving the optimal concentration required for maximal T_c [247].

In lead cuprates of the $\text{Pb}_2\text{Sr}_2(\text{Ln}, \text{Ca})\text{Cu}_3\text{O}_{8+\delta}$ (2213) type, increasing the oxygen content of the material by annealing in an oxygen atmosphere oxidizes the Pb^{2+} and Cu^{1+} without affecting the CuO_2 sheets, which governs the superconductivity in this material [248]. Though this system shows a wide range of oxygen stoichiometry (associated with a structural phase transition from orthorhombic to tetragonal symmetry), maximum T_c is observed for any given composition where δ is close to zero [249]. Samples with $\delta \approx 0$ are therefore prepared by annealing in a nitrogen atmosphere containing little oxygen. The lead 1212 cuprates, on the other hand, are best prepared in a flowing oxygen atmosphere. The samples obtained after the oxygen treatment are often not superconducting since there is an oxygen excess. The samples are quenched in air at around 1073 K in order to achieve superconductivity [250].

Superconducting properties of the electron-doped superconductors, $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-x}$, are sensitive to the oxygen content. The as-prepared samples which are semiconducting have oxygen content greater than four. Samples with oxygen content less than four are obtained by annealing in a reducing atmosphere (N_2 , Ar or dilute H_2) at around 1173 K. Maintaining the oxygen stoichiometry at less than four is essential for having an oxidation state of Cu less than 2+ in this material [25].

9. Concluding remarks

In the earlier sections we presented details of the preparative methods for the synthesis of various families of cuprate superconductors. In addition, we also examined the advantages and disadvantages of the different methods. Since more than one method of synthesis has been employed for preparing any given cuprate, it becomes necessary to make the right choice of method in any given situation. In order to assist in making such a choice, we have tabulated in table 6 the important preparative methods employed to synthesize some of the representative cuprates, where the recommended methods are also indicated.

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